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# (54) Process for bonding germanium to metal

(57) A germanium component is bonded to a second component of metal, or metal-surfaced ceramic, by a braze composed of a first metal, which is constituted by or deposited on the surface of the second component, one or two additional metals deposited on one or both or inserted between the component surfaces, and germanium derived from the germanium component, the additional metal or metals and germanium preferably forming a eutectic which interacts with the first metal to form a molten braze at a temperature below the melting points of the components. Specifically, for the manufacture of an infra-red transmitting window for a laser, a germanium window 1, 2 is bonded to a support 3 of Nilo K or Kovar (Registered Trade Marks) by coating the latter at 6 with nickel or cobalt, introducing silver and/or copper either as coatings 7, 8 on, or as a shim(s) powder or wire, inserted between, the mating surfaces, and heating the assembly in a vacuum furnace. The braze withstands temperatures used for outgassing the device. Gold and tin are referred to also as additional metals.

Fig. 2.

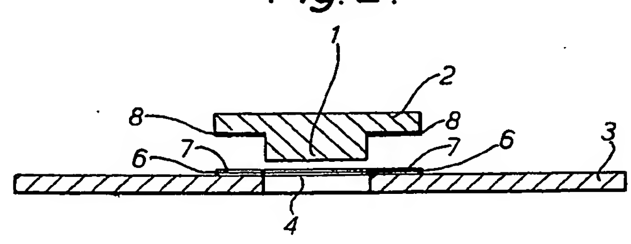


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Fig.1.

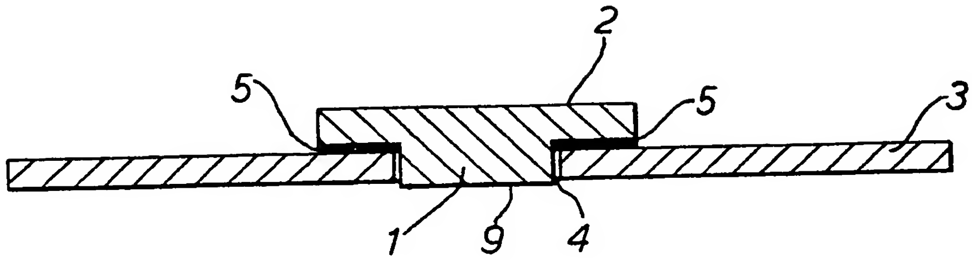
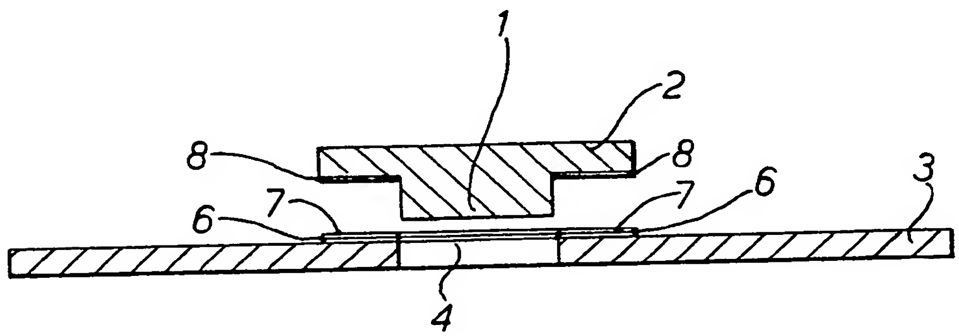



Fig.2.



SPECIFICATION

**Process for bonding germanium to metal**

This invention relates to a process for bonding a germanium component to a metal or alloy surface of a second component, and is also concerned with composite articles and devices which include a component of germanium and a metal- or alloy-surfaced component bonded together by the process described.

The bonding of a germanium component to a component formed of, or having a surface layer composed of, a metal or alloy may be required, for example, in the manufacture of a semiconductor device. In another type of application of germanium, which utilises its property of transparency to infra-red radiation of some wavelengths, it may be employed for forming infra-red transmitting windows in some radiation-emitting or collecting devices. For example, germanium may be used to form a partially reflecting mirror in a laser, for transmitting infra-red radiation of desired wavelengths and reflecting radiation of other wavelengths. For such applications, the germanium component is required to be mounted on, and bonded to, a metallic supporting component, which is sealed into an aperture in the main body of the device or may itself constitute the main body of the device: it is usually desirable that the germanium component and its metal support should have substantially matching thermal expansion characteristics in order to minimise stresses generated by differential expansion between these components when they are subjected to changes in temperature in manufacture or use of the device.

It is an object of the present invention to provide a process for forming a vacuum-tight bond, capable of withstanding elevated temperatures without rupturing or undergoing any undesirable physical or chemical changes, between a germanium component and a metal or alloy surface of a second component.

According to the invention, a process for bonding a first component composed of germanium to a second component of which at least that portion of the surface to be bonded to the germanium is composed of a metal or alloy includes the steps of providing a first metal surface which is constituted by, or forms a continuous adherent coating on, the said surface portion of the second component, introducing not more than two additional metals between said first metal surface and that portion of the surface of the germanium component which is to be bonded to the second component, the said first metal and additional metal or metals being so chosen that interaction can occur between the said metals and germanium to form a molten braze composition at a temperature which is appreciably lower than both the melting points of germanium and of the metal or alloy of which the second component or the said surface portion thereof is composed, and is appreciably higher than any temperature to which the bonded components will subsequently be subjected, and brazing the components together by heating the assembly of said components and first and additional metals, while under light pressure, to a sufficiently high temperature to cause the said interaction to take place and then cooling the assembly to cause the molten braze composition so formed to solidify.

The term "bond surface" of a component will hereinafter be employed to refer to that portion of the surface of the component which is to be bonded to a portion of the surface of the other component.

An additional metal may be introduced by forming a coating thereof on said first metal surface, and/or on the bond surface of the germanium component, or may be provided as a separate metal body, suitably in the form of a shim, powder or wire, which is inserted between the first metal surface of the second component and the bond surface of the germanium component. Alternatively, where two additional metals are employed, the first metal surface may be coated with one of the additional metals, and the second additional metal may be introduced either as a coating on the germanium component or as a separate metal body as aforesaid; or both additional metals may be inserted between the components.

The metals employed for interacting with the germanium to produce the braze composition should be such that the brazing procedure does not result in the formation of any undesirable reaction products, such as intermetallic compounds having characteristics liable to adversely affect the bond. Examples of suitable metals for forming the braze are, as said first metal, nickel or cobalt, and as said additional metal or metals, silver and/or copper.

The said second component may be wholly composed of a metal or alloy; aternatively, the process of the invention may be used for bonding a germanium component to a component of non-metallic, for example ceramic, material at least part of whose surface has been metallised in known manner.

For forming a satisfactory bond which will be free from stress over a wide temperature range, it is usually preferred that the said second component has thermal expansion characteristics substantially matching those of germanium. However, in some cases, where the portion of the second component to be bonded to the germanium is a thin member, such as a feather-edge portion, of ductile metal, some degree of expansion mismatch may be acceptable.

In some cases, where the said second component, or the bond surface thereof, is composed of a single metal which is suitable as a constituent of the braze composition, such as nickel or cobalt, and the second component either has a thermal expansion coefficient substantially matching that of germanium or is in the form of a thin ductile metal member as aforesaid, a said additional metal coating may be deposited directly on the bond surface of this component, the bond surface metal thus constituting the said first metal. However, in other cases, where the second component or its bond surface is composed of an alloy or of a metal which is not suitable for incorporation in the braze, a coating of a

suitable first metal is deposited on the bond surface of the component. Where the second component, or metallised surface thereof, is composed of an alloy, the said first metal coating is preferably a constituent of the alloy. One class of alloys particularly suitable for bonding to germanium, since they have thermal expansion coefficients substantially matching that of germanium, consists of alloys composed mainly of nickel, cobalt and iron, such as those identified by the Registered Trade Marks "Nilo K" and "Kovar": the bond surface of a component formed of an alloy of this type is suitably first coated with nickel or cobalt.

The additional metal (or each additional metal if two metals are used) is preferably one which forms an eutectic with germanium, which eutectic will interact with the said first metal on the second component to form a liquid phase braze composition at a suitable temperature as aforesaid, the eutectic being the predominant constituent of the braze. Metals which combine with germanium to form eutectics capable of interacting with nickel or cobalt to produce molten braze compositions at appropriate temperatures, and which may therefore be used as the additional metal or metals, include silver, copper, gold and tin, the gold- and tin-containing compositions being molten at somewhat lower temperatures than the compositions containing silver and copper. For example, silver and germanium form an eutectic, containing 19% of germanium, at 651°C, and this eutectic interacts with nickel or cobalt to form a molten braze composition at a slightly lower temperature; similar results are obtained if silver is replaced by copper.

A first metal coating on the bond surface of the second component, in addition to contributing to the braze composition, forms a barrier layer between the underlying metal or alloy structure and the braze, preventing the incorporation of any underlying metal in the braze and thus simplifying the metallurgical constitution of the braze by minimising the number of constituents therein, and in some cases preventing the formation of an alloy having unsuitable properties, for example having an undesirably low melting point. For example, a coating of nickel or cobalt on Nilo K or Kovar prevents the formation of a low melting alloy of the silver-germanium eutectic with iron, nickel and cobalt.

The metal coatings and/or inserted metal bodies should be in as pure a form as possible, but it will be understood that the presence in these coatings of small amounts of incidental alloying constituents and impurities, which have no deleterious effect on the bond, is permissible. A coating or coatings on the second component may conveniently be deposited by electroplating. If it is desired to apply a coating of an additional metal to the germanium component, this can in some cases be done by electroplating, but usually, especially if the germanium is of high purity, other metallising processes such as evaporation or sputtering, or application of the metal as a paint, will give more satisfactory results. If desired, an evaporated or sputtered film may be thickened by subsequent electro-plating. The metal coatings or inserts can be of any convenient thickness, but where the first metal is in the form of a coating on the second component the relative thicknesses of this coating and of the additional metal coating(s) or inserts(s) should be such that a part of the first coating remains, between the initial component surface and the braze, after completion of the brazing operation, to form a barrier layer as aforesaid. For example, typical thicknesses may be from 25 to 50 microns for a first metal coating on the second component, and a total of 20 to 40 microns for the additional metal or metals.

The said first metal and additional metal or metals should have low vapour pressures, in view of the elevated temperatures employed for forming the bonds, and the possibility of the bonds being subsequently subjected to high temperatures. These metals should also be resistant to atmospheric corrosion; however, the heating procedure for forming the braze is preferably carried out in vacuum. On completion of the heat treatment, the assembly is preferably allowed to cool slowly to room temperature, suitably by retaining it in the furnace while the latter cools, or by appropriate programming.

Some specific processes, in accordance with the invention, for bonding a germanium component to a component composed essentially of a nickel-cobalt-iron alloy, which we have carried out, will now be described in the following examples.

*Example 1*

For the preparation of a tensile test specimen consisting of a slice of germanium, 10 mm square and 0.5 mm thick, bonded to two strips of Nilo K each 50 mm long, 12 mm wide and 0.7 mm thick, the strips were electroplated, each on an end portion of one face, first with cobalt to a thickness of 50 microns, then with a 15 microns coating of silver, and a coating of silver 12 microns thick was applied to both faces of the germanium slice, also by electroplating. The three components were assembled to form a lapped specimen, with the silver-coated germanium slice sandwiched between the over-lapping coated end portions of the Nilo K strips, and the assembly was heated in a vacuum furnace to a maximum temperature of 680 - 690°C, the time for which the assembly was maintaind above 650°C (that is to say approximately the silver-germanium eutectic temperature) being 20 minutes. The assembly was then allowed to cool slowly to room temperature in the furnace.

*Example 2*

A procedure similar to that described in Example 1 was used to prepare a test specimen in which copper was employed instead of silver for coating the germanium slice and the cobalt-plated portions of the Nilo K strips.

*Example 3*

A test specimen similar to that described in Example 1 was prepared by a similar procedure, except that the end portions of the Nilo K strips were first plated with nickel instead of cobalt, these portions of the strips, and both faces of the germanium slice, then being plated with silver.

*Example 4*

A test specimen of the form described in Example 1 was prepared in the same manner, but using nickel for the first coating on the end portions of the Nilo K strips, and copper for the second coating on the strips and for the coating on both faces of the germanium slice.

A number of specimens were prepared as described in each of the above examples, and the peak temperatures attained during the heating procedures were all in the range of 650°C to 750°C, in each case the assembly being maintained above the silver-germanium or copper-germanium eutectic temperature for 10 to 30 minutes, the longer times being associated with the higher peak temperatures.

The tensile strengths of the composite Nilo K-germanium specimens prepared as described in the above examples were measured at 500°C, and in all cases were found to be in the range of 8 to 11 meganewtons per square metre. This showed that the bonds formed between germanium and Nilo K possessed adequate strength to withstand the temperatures of 400 - 500°C which are typically employed for the vacuum baking of various devices, in the manufacture thereof, for outgassing.

It will be understood that the Nilo K components used in the processes of the examples can be replaced by components of Kovar or any other similar nickel-iron-cobalt or nickel-iron alloy having substantially the same thermal expansion characteristics, or by, for example, ceramic components with bond surfaces metallised with such alloys, with similar results.

One specific form of composite article, which can be formed by bonding together a germanium component and a nickel-cobalt-iron alloy component by any of the methods described in the above examples, is shown in the accompanying diagrammatic drawing, and consists of a germanium window mounted on a metallic support for incorporation in the casing of a gas waveguide laser. In the drawing,

*Figure 1* shows the completed composite article in sectional elevation, and

*Figure 2* shows, also in sectional elevation, the germanium and metal components before they have been bonded together.

The germanium component is in the form of a cylindrical block 1 with a flange 2, and the metal component is a disc 3 of, for example, Nilo K or Kovar, with a central aperture 4, into which the germanium block 1 is inserted, the flange 2 being bonded to the surface of the disc 3 around the aperture, as shown at 5 in Figure 1.

One method of forming the bond is shown in Figure 2: the edge region of the disc 3 surrounding the aperture is first electroplated with nickel or cobalt, 6, and then with silver or copper 7, and a coating 8, of either the same metal as that of the coating 7 or the alternative metal, is deposited on the mating surface of the flange 2 of the germanium component, by electroplating or by other suitable means. The thicknesses of the metal coatings are suitably as described above in Example 1. The coated surfaces of the two components are then placed in contact, the components being held together under a small load, and the resulting assembly is heated as described in Example 1 to form the bond 5.

In an alternative method of forming the bond, instead of applying coatings of silver or copper to the nickel- or cobalt-coated portion of the disc 3 and to the flange 2 of the germanium component, silver and/or copper in the form of a shim or shims, powder or wire may be inserted between the mating portions of the components.

In the manufacture of a laser incorporating a germanium window of the form shown in the drawing, the alloy disc 3 is sealed into an aperture in a stainless steel casing (not shown in the drawing), by a known welding technique, in such a position that the surface 9 (Figure 1) of the germanium component is located at one end of the laser waveguide (not shown), the disc 3 thus constituting part of the casing with the flange 2 of the germanium component lying on the exterior thereof. The completed device is finally outgassed by baking at 400°C in vacuum, no deterioration of the germanium-metal bond being detected.

The germanium-metal bonding process of the invention has the additional advantage that, since it is a reactive brazing process, the use of a flux is not usually necessary. Furthermore since the braze material is of metallurgically simple constitution having only three or four constituents, the brazing process is easy to control in comparison with a system having a larger number of constituent metals.

CLAIMS

1. A process for bonding a first component composed of germanium to a second component of which at least that portion of the surface to be bonded to the germanium is composed of a metal or alloy, which process includes the steps of providing a first metal surface which is constituted by, or forms a continuous adherent coating on, the said surface portion of the second component, introducing not more than two additional metals between said first metal surface and that portion of the surface of the germanium component which is to be bonded to the second component, the said first metal and additional metal or metals being so chosen that interaction can occur between the said metals and germanium to form a molten braze composition at a temperature which is appreciably lower than both the melting points of germanium and of the metal or alloy of which the second component or said surface portion thereof is composed, and is appreciably higher than any temperature to which the bonded components will subsequently be subjected, and brazing the components together by heating the assembly of said components and first and additional metals, while under light pressure, to a sufficiently high temperature to cause the said interaction to take place and then cooling the assembly to cause the molten braze composition so formed to solidify.

2. A process according to Claim 1, wherein the second component is wholly composed of a metal or

alloy having thermal expansion characteristics substantially matching those of germanium.

3. A process according to Claim 1, wherein the second component is composed of non-metallic material having thermal expansion characteristics substantially matching those of germanium, at least part of the surface of which has been metallised.

4. A process according to Claim 1, wherein the portion of the second component which is to be bonded to the germanium component is a thin member composed of ductile metal.

5. A process according to Claim 2, 3, or 4, wherein the second component or said surface portion thereof is composed of a metal which is suitable as a constituent of the braze composition and which constitutes the said first metal.

6. A process according to Claim 1, 2, 3 or 4, wherein the second component or said surface portion thereof is composed of an alloy or of a metal which is unsuitable as a constituent of the braze composition, and a coating of said first metal is deposited on said surface portion of the second component.

7. A process according to Claim 6, wherein the second component is composed of an alloy, and the said first metal coating is a constituent of the alloy.

8. A process according to Claim 7, wherein the second component is composed of an alloy consisting mainly of nickel, cobalt and iron, and the said first metal coating consists of nickel or cobalt.

9. A process according to any preceding Claim, wherein a said additional metal is introduced by forming a coating thereof on the said first metal surface portion of the second component.

10. A process according to any preceding Claim, wherein a said additional metal is introduced by forming a coating thereof on the said surface portion of the germanium component.

11. A process according to any of the preceding Claims 1 to 8, wherein a said additional metal is introduced by inserting a separate body of said metal between the first metal surface portion of the second component and the said surface portion of the germanium component.

12. A process according to any preceding Claim, wherein the said additional metal, or each additional metal, is a metal which forms with germanium an eutectic capable of interacting with the said first metal to form a said braze composition.

13. A process according to Claim 12, wherein the said first metal is nickel or cobalt, and the said additional metal, or each additional metal, is one of the metals silver, copper, gold or tin.

14. A process according to Claim 6, 7 or 8, wherein the relative thicknesses of the first metal coating on the second component and of the additional metal coating or coatings or insert or inserts are such that a part of the first metal coating remains, between the initial second component surface and the braze, after completion of the brazing operation, to form a barrier layer between the braze and the underlying metal structure of the second component.

15. A process according to Claim 14, wherein the thickness of the first metal coating on the second component is from 25 to 50 microns, and the total thickness of the additional metal or metals is from 20 to 40 microns.

16. A process according to Claim 1, for bonding a germanium component to a component composed essentially of a nickel-cobalt-iron alloy, or of a ceramic material having at least a said surface portion metallised with a said alloy, carried out substantially as hereinbefore described in any one of the Examples 1 to 4.

17. A process according to Claim 1, for the manufacture of a composite article by bonding together a germanium component and a nickel-cobalt-iron alloy component, substantially as hereinbefore described with reference to the accompanying drawing.

18. A composite article consisting of a germanium component and a second component of which at least that portion of the surface which is bonded to the germanium component is composed of a metal or alloy, which article has been manufactured by a process according to any preceding Claim.

19. A device incorporating a composite article according to Claim 16.

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